

The monosubstituted thio-imidazolones, where the methylene hydrogen has been replaced, yielded in every case thio-ethers.

The hydrolysis of certain of these imidazolones has been studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

POTASSIUM AZIDO-DITHIOCARBONATE¹

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(With Notes on Crystallography by A. C. GILL)

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In connection with an investigation of the imide character of hydronitric acid, F. Sommer² succeeded in preparing and analyzing the hydrated sodium and barium salts of a new acid, which he named azido-dithiocarbonic acid. These compounds were shown to have the formulas $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Ba}(\text{SCSN}_3)_2 \cdot 5\text{H}_2\text{O}$. When the attempt was made by Sommer to prepare the corresponding potassium salt by a similar method, the crystalline product that he obtained exploded with violence as he spread it carefully, with the aid of a porcelain spatula, upon a porous plate, thus deterring him from further work upon this compound.

The formation of potassium azido-dithiocarbonate has been shown by the authors of the present paper³ to take place slowly, even at ordinary temperatures, when carbon disulfide is brought into contact with aqueous solutions of potassium trinitride. It has, moreover, been demonstrated that an important catalytic effect is exerted by this azido-salt in the reaction between aqueous solutions of potassium trinitride and iodine in presence of carbon disulfide. In this connection it has been found necessary to prepare and analyze the azido salt, and to study certain of its properties and reactions.

Method of Preparation.—A sample of pure potassium trinitride weighing 6 g. was dissolved in 25 cc. of distilled water, and the resulting solution, in a 100cc. glass bottle, was treated with about 6 g. of pure, redistilled carbon disulfide, an amount slightly in excess of that required for the ratio $\text{KN}_3 : \text{CS}_2$. The tightly corked bottle containing the reacting mixture was held at a temperature of about 40° in a water-bath, with occasional shaking, until the carbon disulfide had entirely disappeared.

A convenient test indicating the completion of this reaction consists in adding a few drops of iodine solution to a small sample of the reacting mix-

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 3 under Heckscher Grant No. 4. For Articles 1 and 2 see *THIS JOURNAL*, **44**, 2106 and 2116 (1922).

² Sommer, *Ber.*, **48**, 1833-41 (1915).

³ Browne and Hoel, *THIS JOURNAL*, **44**, 2109 (1922).

ture. Immediate discharge of the iodine color, unaccompanied by perceptible evolution of nitrogen, conclusively proves absence of unchanged potassium trinitride, as this substance would be quickly decomposed by the iodine, in presence of the azido salt, with quantitative liberation of nitrogen.

The solution of potassium azido-dithiocarbonate obtained by this method was concentrated over phosphorus pentoxide in a vacuum desiccator, almost to the point of saturation, and was then filtered carefully to remove free sulfur. The clear filtrate was slowly cooled over ice until the formation of crystals took place. The crystals were cautiously removed, and were dried, first between filter paper, later on a porous plate, with the aid of a bone spatula, and finally in a vacuum over phosphorus pentoxide. Failure of the crystals, after thorough drying between filter paper, to lose appreciable weight when stored in a vacuum over phosphorus pentoxide for 60 hours, corroborated at the outset the opinion of Sommer that the potassium salt, unlike the salts of sodium and barium, ordinarily crystallizes from aqueous solution in the anhydrous condition, a fact that has been verified repeatedly in subsequent work.

Analysis.—Carefully dried samples of potassium azido-dithiocarbonate prepared by the foregoing method were analyzed as follows. The potassium was determined by heating weighed samples of the compound with sulfuric acid, and weighing the potassium sulfate formed.

Subs., 0.1677, 0.3381; K_2SO_4 , 0.0932, 0.1889. Calc. for $KSCSN_3$: K, 24.86. Found: 24.94, 25.07.

The sulfur was determined by oxidizing weighed samples of the salt with conc. nitric acid and bromine, and weighing the sulfur in the form of barium sulfate.

Subs., 0.4502, 0.4669; $BaSO_4$, 1.3550, 1.3942. Calc. for $KSCSN_3$: S, 40.78. Found: 41.34, 41.01.

The nitrogen was determined by combustion of the azido salt with copper oxide in a current of pure carbon dioxide. The explosive character of the salt necessitated admixture with precipitated silica and with copper oxide in finely divided form. The mixture was distributed through the combustion tube over a length of about 25 cm.

Subs., 0.1343, 0.1629; N_2 , 28.53 cc. (0.03568 g.), 34.75 cc. (0.04346 g.). Calc. for $KSCSN_3$: N, 26.73. Found: 26.57, 26.68.

Crystallographic Data.—Samples of the white crystals were submitted to Professor A. C. Gill of the Department of Geology of Cornell University, who makes the following statement concerning their properties.

“The crystals examined presented quite variable habitus, though tabular development with 4-sided or 6-sided outlines was most common. The 6-sided crystals usually showed elongation parallel to the direction which may be designated in this description as the macro-axis, though accurate determination of the crystallographic constants was rendered impossible, with the apparatus at hand, by the rather rapid deliquescence

which the substance undergoes. The 4-sided crystals gave angles of very nearly 87° and 93° on the stage of a petrographic microscope. This would indicate an axial ratio of $a:b = 0.95:1$. Not even approximate measurements of the length of "c" axis were obtained. Reticulated masses very like the well-known occurrence of lead carbonate in nature were frequently observed under the microscope on evaporating the liquid in which the azido-salt had been formed on a warm glass slide. Five-sided crystals, bounded by the prism and one face of the macro-pinacoid, were rather frequently observed but, on the whole, this was not thought to indicate a hemimorphic symmetry, as the parallel face was usually observable unless the development of the one face was rather small. The optical behavior of the tabular crystals is the best argument for their rhombic character. They show parallel extinction in all positions, even in the reticulated masses. They are optically biaxial with a large angle, $2V$, greater than 75° . The axis of greatest elasticity bisects the acute angle of the prism, while the axis of least elasticity is normal to the tabular face (001). The optical character seems to be positive, though there is a possibility that the optical angle as seen in the ordinary position is greater than 90° , in which case the crystals are negative.

"Double refraction is rather strong, estimated at 0.050, and dispersion is very unusual. From the peculiar purple appearance of the first order red interference color it would appear that the birefringence for red light is much stronger than for blue, so that a thickness of crystal producing 200 to 230μ retardation for the blue end of the spectrum produces something like twice that amount for the red end. Careful study of the substance by monochromatic light would be necessary to confirm the accuracy of this explanation."

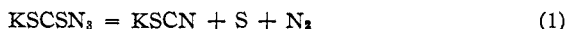
Solubility.—Potassium azido-dithiocarbonate is very soluble in water, and deliquesces rapidly under ordinary atmospheric conditions. No accurate determination of the solubility was made, partly because of risk attending the use of relatively large amounts of this explosive substance. As a first approximation, however, small samples of the salt were weighed on watch crystals. These were again weighed just as the last crystal was dissolving in the moisture condensed from the atmosphere. Samples weighing 0.0225 and 0.1720 g. were found to dissolve in 0.0049 and 0.0381 g. of water. One part of water will, therefore, dissolve about 4.5 parts of the azido-salt.

When brought into contact with various non-aqueous liquids, all strictly anhydrous, the azido salt was found to be fairly soluble in both methyl alcohol and acetone, very slightly soluble in ether, and practically insoluble in ethyl alcohol, benzene, carbon tetrachloride, carbon disulfide, and chloroform.

Decomposition.—The azido salt is rather sensitive to shock. Dry crystals have repeatedly been broken in an agate mortar, but during this operation several samples have exploded with violence. The explosion experienced by Sommer on rubbing the moist crystals upon a porous plate was undoubtedly due to the sensitizing action of the sharp edges of the plate.

When heated slowly in a capillary melting-point tube, the crystals began to decompose at about 126° , with evolution of gas. When heated rapidly upon an iron plate the substance detonates with a sharp explosion, but less

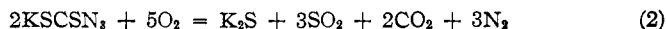
violently than do the heavy metal trinitrides. Slow thermal decomposition of potassium azido-dithiocarbonate takes place quantitatively in accordance with the equation.



Samples of the azido salt weighing 0.1296 and 0.1405 g. held at 100° for about 50 hours in a nitrometer tube yielded 17.64 and 19.01 cc. (corr.) of nitrogen, corresponding to 1.91 and 1.90 atoms of nitrogen per molecule of the salt. Titration of the aqueous extract of each residue with standard silver nitrate solution showed the presence of 0.0793 and 0.0869 g. of potassium thiocyanate, or 0.99 and 1.00 molecule of this substance per molecule of azido salt.⁴

The final residues obtained after the extraction consisted of 0.0237 and 0.0245 g. of free sulfur, corresponding to 0.90 and 0.86 atoms of sulfur per molecule of the salt. The low values for sulfur are attributable to unavoidable loss of small amounts of that substance by sublimation during the long period of heating in the nitrometer.

When the azido-salt explodes in the open air a spectacular flame is produced, with liberation of much heat and formation of numerous products. Samples of the compound weighing 0.2 g. and held in a deflagrating spoon suspended in the center of a 12-liter Pyrex glass flask were detonated by means of an electric spark. The presence of sulfur dioxide, carbon dioxide, hydrogen sulfide, sulfur trioxide, free sulfur, and potassium thiocyanate as products of the decomposition in addition to nitrogen was established. The principal reaction may therefore be expressed by the equation,



although a part of the sample undoubtedly decomposes in accordance with Equation 1.

Aqueous solutions of the azido salt are quite stable at temperatures of 10° or lower, as is also the dry salt itself. At somewhat higher temperatures, however, the aqueous solutions gradually become turbid, with separation of sulfur, liberation of nitrogen, and formation of potassium thiocyanate. A solution obtained by dissolving 0.1870 g. of the salt in 10 cc. of water, and held in a Lunge nitrometer at 20–25° gradually became turbid, and liberated in 16 days 2.44 cc. (corr.) of nitrogen. Samples of the dry salt stored in the desiccator at room temperatures gradually turn yellow, owing to the separation of sulfur.

When a solution of the azido-salt was subjected to distillation thiocyanates were obtained in the residue, but no appreciable quantities of cy-

⁴ In connection with certain of the earlier experiments the presence of potassium thiocyanate among the products of decomposition of the azido salt was established by microchemical tests performed by Professor E. M. Chamot, of whose work the authors desire to express their appreciation.

nides, sulfides, sulfites, carbonates, trinitrides, or of ammonia were found in either distillate or residue. When 15 cc. of an approximately 20% solution of the azido salt was mixed with an equal volume of 6 *N* potassium hydroxide solution, and distilled until half of the volume had gone over, thiocyanates were found in the residue. With 6 *N* sulfuric acid in place of the alkali, both thiocyanates and sulfides were found in residue and distillate. In a blank experiment with potassium thiocyanate and sulfuric acid similar results were obtained. In no case were cyanides, sulfites, carbonates, trinitrides, or ammonia detected.⁵

Small amounts of a solution of potassium azido-dithiocarbonate were added to aqueous solutions of silver, mercurous, mercuric, bismuth, cupric, cadmium, aluminum, chromium, nickel and cobaltous nitrates; ferrous, ceric, zinc, and thallosulfates; stannous, and manganous chlorides; lead, and cupric acetates, and qualitative observations were made which, in the main, corroborate the work done by Sommer with a solution of the sodium salt, in investigating the properties of the azido-dithiocarbonate ion.

Solutions of potassium azido-dithiocarbonate, when treated with certain oxidizing agents yield a white precipitate of azido-carbondisulfide, $(SCSN_3)_2$. It was found by Sommer that solutions of (a) iodine in potassium iodide, (b) ferric chloride, (c) potassium permanganate, potassium dichromate, and ceric salts in presence of sulfuric acid, behave in this manner. These results have been confirmed by the authors,⁶ and additional oxidizing agents, including potassium persulfate, hydrogen peroxide, bromine water, chlorine water, as well as sodium nitrite, manganese dioxide in sulfuric acid solution, and stannic chloride in hydrochloric acid solution, have been found to react at room temperature with solutions of the azido salt, precipitating azido-carbondisulfide. Potassium iodate reacts slowly, after standing for several hours, while ozone yields no precipitate whatever. Anodic oxidation of the azido salt in aqueous solution readily yields azido-carbondisulfide.

Structure.—The fact that potassium azido-dithiocarbonate decomposes quantitatively when gently heated, into potassium thiocyanate, sulfur, and nitrogen affords almost conclusive proof of the correctness of the structure assigned by Sommer to salts of azido-dithiocarbonic acid. If the correctness of the Angeli-Thiele-Turrentine formula for hydronitric acid be assumed, the structure of potassium azido-dithiocarbonate is as follows: $K-S-C(=S)-N=N\equiv N$.

⁵ These and certain other qualitative tests, connected with the present investigation, were performed by Miss Hazel E. Braman, to whom the authors wish hereby to express their gratitude.

⁶ In connection with this work the authors acknowledge with pleasure the assistance rendered by Mr. A. L. Satterthwaite.

Summary

1. Potassium azido-dithiocarbonate, found by analysis to have the formula $KSCSN_3$, may be prepared by the action of carbon disulfide upon potassium trinitride in aqueous solution.

2. The colorless, unstable, deliquescent crystals of this azido salt decompose quantitatively when gently heated, yielding potassium thiocyanate, sulfur and nitrogen, or explode when rapidly heated, with formation of potassium sulfide, carbon dioxide, sulfur dioxide and trioxide in addition to these products.

3. Solutions of the azido salt when treated with various oxidizing agents, or when subjected to electrolysis yield azido-carbonylsulfide, $(SCSN_3)_2$.

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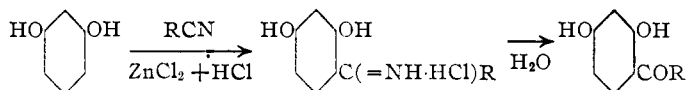
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

CONDENSATION OF CERTAIN NITRILES AND VARIOUS POLY-HYDROXYPHENOLS TO FORM PHENOLIC ACIDS

By WILSON D. LANGLEY WITH ROGER ADAMS¹

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From the time Hoesch² first discovered that nitriles reacted with certain phenols in the presence of anhydrous zinc chloride and dry hydrogen chloride to give ketones according to the following equations



this reaction has been applied extensively in organic chemistry. It has proved of particular value in the synthesis of various natural products, in the preparation of certain synthetic drugs, in the formation of coumarones, and various other types of ketones and aldehydes.³

Another application of this reaction, namely, the condensation of β -chloro-propionitrile with resorcinol to prepare 7-hydroxychromanone-4 was tried as follows:

¹ This communication is an abstract of a thesis submitted by W. D. Langley in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Hoesch, *Ber.*, **48**, 1122 (1915).

³ (a) Hoesch, *ibid.*, **50**, 462 (1917). (b) Sonn, *ibid.*, **50**, 1262 (1917); (c) **51**, 821, 1829 (1918); (d) **52**, 923 (1919). (e) Stephen, *J. Chem. Soc.*, **117**, 309, (f) 1529 (1920), (g) Karrer, *Helvetica Chim. Acta*, **2**, 89, 462, 486 (1919); **3**, 261, 392, 541 (1920); **4**, 203, 707 (1921). (h) Fischer, *Ber.*, **50**, 611, 693 (1917). (i) Bauer, *Arch. Pharm.*, **259**, 53 (1921).